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**Title
Glass Corrosion in Natural Environment**

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Abstract .

A series of studies of the effects of solutes which appear in natural aqueous environments, specifically Mg and Al, under controlled conditions, permit characterization of the retardation of silicate glass leaching in water containing such solutes. In the case of Mg the interaction with the glass appears to consist of exchange with alkali ions present in the glass to a depth of several microns. The effect of Al can be observed at much lower levels, indicating that the mechanism in the case of Al involves irreversible formation of aluminosilicate species at the glass surface.

SILICA GLASS
LEACHING
AQUEOUS SOLUTIONS
MAGNESIUM
ALUMINUM
CORROSION RESISTANCE

ALKALINITY
SURFACE REACTIONS
PIT
CHEM. SORPTION
MAGNETIC PERMEABILITY

I. Leach Studies

GENERAL

The experimental program described below was designed to characterize the effects of solutes common in natural water environments, in particular Mg and Al, on the durability of silicate glasses exposed to such environments. Two types of experiments were included in the program. The first consisted of exposing a glass to an aqueous medium containing a desired level of Mg and Al and replacing the leachate at specified time intervals with the same volume of fresh leachant. This type of experiment is expected to simulate the actual long-term behavior of glass exposed to flowing water, e.g. in a sub-seabed or terrestrial porous rock formation. The second type of experiment was based on pre-treatment of the glass with Mg or Al solutions followed by testing of its durability in de-ionized water or buffered solutions in the absence, of solutes, in order to obtain an immediate indication of the effects of Mg and Al on the subsequent reactivity of the glass surface sites. In both sets of experiments de-ionized water as well as buffered solutions were used as leaching media; the latter with a view to separating solute effects on glass durability from pH effects.

EXPERIMENTAL PROCEDURES AND RESULTS

A. Replenishment Experiments

1. Leaching of Soda-Lime Glass in Unbuffered Mg solutions

Experiment designation: 5092/89/85/86/87/88

Leachants: 0, 1.2, 4, 13, 40, 400 mg/L Mg in de-ionized water
(introduced as $\text{MgCl}_2 + \text{MgSO}_4$)

Glass: Soda-lime (Table 1)

Sample geometry: Wafers

S/V: 20 m^{-1} (8 $\text{cm}^2/40 \text{ mL}$)

Temperature: 90 C

Leachant exchange frequency: Daily for the first 3 days, twice weekly for 1 week, weekly for 12 weeks, monthly thereafter.

Initiation date: March 23, 1988

The leachate compositions at the end of the 6th monthly exposure period (days 245-263) are given in Table 2. The dependence of Si leachate concentrations on time is shown in Figure 1.

2. Leaching of Pyrex Borosilicate Glass in Borate-Buffered Mg Solutions

Experiment designation: S121/122/123/124

Leachant: 0, 0.1, 1, 10 mg/L Mg in 0.04 M pH 8.1

Tris (hydroxymethyl) aminomethane buffer (Mg introduced as $\text{Mg}(\text{NO}_3)_2$)

Glass: Pyrex (Table 1)

Sample geometry: -40+60 mesh (250-355 microns) powder

S/V: 290 m^{-1} (0.9 g or 87 $\text{cm}^2/30 \text{ mL}$)

Temperature: 90 C

Leachant exchange frequency: Daily for 2 days; twice weekly for 1 week; weekly thereafter.

Initiation date: October 19, 1988

The leachate compositions at the end of the 12th weekly exposure period (days 85-92) are given in Table 3.

3. Leaching of Soda-Lime Glass in Buffered Al Solutions

Experimental Designation: S130/131/132/133/134

Leachant: 0.04 M pH 9.5 CAPS (3-cyclohexylamino-1-propane-sulfonic acid) buffer (Al introduced as $\text{Al}(\text{NO}_3)_3$)

Glass: Soda-lime (Table 1)

Sample geometry: -40+60 mesh (250-355 micron) powder

S/V: 290 m^{-1} (0.9 g or 87 $\text{cm}^2/30 \text{ mL}$)

Temperature: 90 C

Leachant exchange frequency: Weekly

Initiation date: December 28, 1988

The leachant compositions at the end of the 6th weekly exposure period (days 35-42) are given in Table 4.

B. Pre-treatment Experiments

Experimental designation: MAM 0, 5.5, 8.1

Pre-treatment:

- (i) None
- (ii) 18 mg/L Mg (as $\text{Mg}(\text{NO}_3)_2$) in 1.0 M pH 5.5 tris buffer, 3.5 g of glass rolled in 200 mL of solution for 3 days at 25 C, filtered, rinsed with 60 mL of water, and dried in a dessicator
- (iii) Similar to (ii), Mg solution buffered with tris (1.0 M) at pH 8.1.

Glasses: Fused quartz, Pyrex borosilicate, soda-lime, Savannah River Laboratory TDS-131, West Valley/ Pacific Northwest Laboratory WV-205 (Table 1)

Leach testing:

Leachant: De-ionized water
Sample geometry: -170+230 mesh (63-90 micron)
S/V: 959 m^{-1} (0.5 g or 192 cm^2 /20 mL)
Temperature: 25 C
Duration: 1 hour
Date: January 19, 1989

The compositions of the spent pre-treatment solutions are given in Table 5. The leachate compositions of the spent pre-treatment solutions are given in Table 6.

LEACH DATA AND EQUIVALENT LAYER THICKNESS

The data obtained in the various leach experiments were processed in order to obtain a quantitative picture of the modification of the glass surface with Mg or Al through sorption or ion exchange as a function of time and its correlation with the evolution of long-term leach rates. The process is illustrated in the case of soda-lime glass in unbuffered Mg solutions (Sections A.1 above). First, the amount of alkalis (Na+K) leached in terms of equivalent thickness (based on the density of alkali oxides in the original glass) was plotted as a function of time, as illustrated for the case of the 40 mg/L Mg leachant in Figure 2. The corresponding accumulation of Mg in the glass surface, assuming the density of sites susceptible to Mg binding to be the density of sites originally occupied by alkalis, is shown in Figure 3. The resulting sorption or exchange isotherm for Mg accumulation in the glass surface as a function of the cumulative concentration of Mg in the aqueous phase is illustrated in Figure 4. The changing leach rates of the glass (based on Si) with time as Mg replaces alkali species are shown in Figure 5 for the 4 mg/L Mg leachant and in Figure 6 for the 40 mg/L Mg leachant. The same leach rates are shown as explicit functions of the amount of Mg accumulated in the glass surface in Figures 9 and 10.

MG AND AL SORPTION: EFFECTS ON GLASS LEACHIBILITY

The experiments described in the present report demonstrate that attenuation of silicate glass leaching takes place in simple solutions containing Mg and Al. The use of simple matrices makes it possible to quantify the effects of Mg and Al more easily, and thus form a basis for interpretation of the leach behavior of glasses in more complicated media such as sea-water and ground-water.

The results of exposure of soda-lime glass samples to various concentrations of Mg (see Table 2), taken at the end of the 6th monthly exchange interval, indicate that a large drop in leach rates occurs as the concentration of Mg in the leachant is raised from 4 to 40 mg/L. It is furthermore observed that over the low Mg range all the Mg in the leachant is still removed by contact with the glass, but at concentration of 40 mg/L Mg the bulk of the Mg in the leachant remains in the aqueous phase, indicating that the glass surface in these cases has become saturated with respect to further Mg uptake. It should be noted that, as documented in Fig. 1, the sharp break in the extent or rate of Si dissolution does not occur at the same Mg concentration throughout the duration of the leach tests. This is also evident in the case where Si leach rates, rather than Si concentrations in the leachates, are plotted as a function of time (Figs. 5-6). This indicates that the rate of surface alteration with Mg depends on the concentration of Mg in the modifying medium. This observation is compatible with the previous finding, viz. that in the case of lower Mg concentrations Mg uptake by the glass is limited by depletion of Mg in the leachant

during exposure. The data in Fig. 4 show the progressive increase in Mg uptake by the glass with increasing cumulative amount of the Mg coming in contact with the glass due to consecutive leachant replenishments. Figs. 7 and 8 show that when Si leach rates are plotted as a function of cumulative Mg uptake rather than time the observed dependence is similar in the cases of high-Mg (40 mg/L) and low-Mg (4 mg/L) leachants, respectively.

The uptake of Mg by the glass can take place through ion exchange with alkalis in the glass surface or through sorption on the surface. According to the data in Figs. 4 and 5, the amount of Mg absorbed over a given period of time is within a factor of 2 of the amount of alkali leached out. This correlation indicates that the major pathway for Mg uptake by the glass involves ion exchange with alkali ions leached out of the glass. Over a period of 100 days at 90 C the equivalent depth of the exchanged layer reaches about 3.5-4 microns (see Fig. 3). According to Figs. 7-8, once this depth is reached the dissolution rate of the glass, based on Si, its major matrix element, drops sharply.

On the other hand, if it is assumed that Mg uptake on the glass surface proceeds through adsorption on the outer glass surface, and that each silicate site on this surface can adsorb a number of layers of Mg ions, the thickness of the sorbed Mg layer covering the outer surface of the glass can be calculated to be approximately 1.5 microns. This thickness corresponds to a scenario of accumulation of thousands of layers of Mg ions on each silicate sites which is much less likely than that of Mg/alkali exchange.

The results obtained in the leach experiments on Pyrex borosilicate glasses in buffered Mg solutions (see Section A.2 and Table 3) generally agree with the results obtained for soda-lime glass. A significant drop in Si leaching is observed at the end of 12 weeks when Mg levels in the leachant are raised from 0-1 to 10 mg/L. Larger differences among the leach rates in leachants with different Mg concentrations may develop as the experiment continues.

The results obtained in the leach experiments on soda-lime glasses in buffered Al solutions (see Sections A.3 and Table 4) again show a sharp drop in Si leaching beyond a certain level of solute, in this case Al, in the leachant. However, in the case of Al the threshold level for the attenuation of leaching is much lower than the corresponding level in the case of Mg. This indicates that in the case of Al the mechanism of surface modification may involve irreversible chemisorption and aluminosilicate group formation rather than reversible ion exchange with alkalis. In practical terms, small amounts of Al in the aqueous phase are much more effective in retarding glass corrosion than corresponding levels of Mg. Further experiments with leachants containing Al are in progress.

The experiments involving leaching in de-ionized water (Table 6) of various glasses previously pre-treated with Mg solutions show that such pre-treatment, too, can lead to higher leach resistance. Analysis of the spent pre-treatment solutions shows no significant differences between the extent of Mg/alkali exchange at pH 5.5 and at pH 8.1, respectively, although the solubility of Mg is much higher at the former pH. Corresponding

dingly, there is no significant difference between the effects of pre-treatment with Mg at pH 5.5 and at pH 8.1, respectively, on the leach resistance of the tested glasses. In general, the pre-treatment with Mg at either one of these pH levels results in a reduction of the subsequent leach rate of the glasses in de-ionized water by a factor of approximately 3. The only exception is the case of fused quartz, where treatment with Mg at pH 8.1 is observed to be much more effective in reducing Si leach rates than a similar treatment at pH 5.5. In the case of fused silica the number of sites occupied by alkalis and available for exchange with Mg ions is very small. As a result, chemisorption and the formation of distinct Mg silicate surface species may have higher relative importance in this case, where the higher effectiveness of pre-treatment at a higher pH can be attributed to the greater stability and lower solubility of Mg silicate species at higher pH levels.

In conclusion, the marked beneficial effects of Mg and Al in the aqueous phase on the leach behavior of glasses can be generally attributed to mechanisms involving ion exchange (except in cases of very low alkali glasses) of Mg or chemisorption and aluminosilicate formation with Al. Experiments leading to quantitative characterization of these phenomena are continuing, intended for instance to explore the reversibility of these processes in the presence of alkalis in the solution. Experiments in buffered media are emphasized in order to separate solute effects from pH effects. In particular, experiments in buffered media are conducted to rule out significant specific

effects of the pH buffers used in the leach studies and permit characterization of the role of the solutes of interest.

II. Surface Studies

The surfaces of glasses leached in aqueous environments with as well as without the presence of Mg^{2+} were studied using an SEM/EDX at the United States Geological Survey in Reston, VA. The results shown in Table 7 represent surface and bulk compositions of soda-lime glasses leached in Mg-containing and Mg-free media, respectively. In experiment A 4-cm² soda-lime glass wafer (see Table 1) was leached in the presence of 1.2 g of -40+60 mesh (250-355 microns) of powder prepared from the same glass in 40 mL of 0.01 M TRIS buffer solution at 90 C. The leachant was exchanged on days 1, 2, 3, 6, 10, 14, 21 and 28 of the test, and then the glass wafer was removed, rinsed quickly with de-ionized water, air-dried, and mounted in epoxy resin for the SEM/EDX measurements. Experiment B was identical with Experiment A, but the leachant in this case also contained 1.6 mg/L Mg, introduced as $Mg(NO_3)_2$. The compositions of each of the two leached glasses were determined in the surface region (approximately 3 microns from the outer glass/water interface) and in the bulk (at a depth of approximately 25 microns), respectively. These results confirm that the extent of leaching, reflected in loss of Na to the aqueous phase, is larger in the case of leaching in de-ionized water than in Mg solutions. Na/Mg exchange in Experiment B is not yet largely reflected in the SEM/EDX results at a depth of 3 microns in accordance with the results of Part I, which show

that exchange at such depth is likely to require exposure durations longer than 28 days.

III. Magnetic Susceptibility of Glasses

A major problem encountered in the production of silicate glasses for nuclear waste immobilization is the development of reliable methods for controlling the production process to ensure that variations in feed stream composition and in melting conditions remain within a region which permits continuous processing at a sufficiently high rate and results in the production of highly durable glasses. Methods of monitoring glass production must be adaptable to the examination of highly radioactive specimens and should be capable of providing data within periods of at most a few hours in order to permit adjustment of feed and melter parameters in time to prevent significant deviations from their desired ranges. Two of the most important properties which characterize glass production are oxidation/reduction state and the extent of crystal formation.

In the present studies, the dc magnetic susceptibility of several glass specimens in the range of interest for nuclear waste immobilization was measured by means of a Faraday balance technique at Howard University. The major-element compositions of these glasses, together with their Fe(II):Fe(III) ratios (wherever available) and extent of devitrification (wherever observed) are given in Table 8. The corresponding dc magnetic susceptibilities at various magnetic field intensities are plotted against the absolute temperature T in Figs. 9a-g, and against $1/T$ in Figs. 10a-g. It is observed that the suscepti-

bility is highest, and shows a relatively weak temperature dependence, in the case of the partially devitrified Glass D. On the other hand, Glass C, which has the highest Fe(II):Fe(III) ratio, exhibits the lowest susceptibility, which is highly dependent of temperature. Magnetic susceptibility measurements, which are relatively simple and rapid, and can be carried out on very small amounts of sample (< 5 mg), may provide, based on the preliminary data obtained so far, very useful data on the oxidation state as well as the extent of crystallization in the course of nuclear waste glass production.

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Table 1.

Soda-lime composition	weight percent
SiO ₂	73.1
Na ₂ O	15.7
CaO	8.9
MgO	3.9
Trace	0.4

Pyrex composition	weight percent
SiO ₂	81
Al ₂ O ₃	2
Na ₂ O	4
K ₂ O	0.5
B ₂ O ₃	13

SRL TDS-131 composition	weight percent
SiO ₂	43.9
Fe ₂ O ₃	13.6
Na ₂ O	12.1
B ₂ O ₃	9.9
MnO ₂	4.5
Li ₂ O	3.7
Al ₂ O ₃	3.7
NiO	2.3
MgO	1.4

WV-205 composition	weight percent
SiO ₂	45.2
Fe ₂ O ₃	11.8
Na ₂ O	11.0
B ₂ O ₃	10.0
K ₂ O	3.5
Al ₂ O ₃	3.3
ZrO ₂	3.1
Li ₂ O	3.1
P ₂ O ₅	2.5
MnO ₂	1.7
MgO	1.3
TiO ₂	1.0

TABLE 2
Leaching of Soda-Lime Glass in Unbuffered Mg Solutions

Leachant composition mg/L	Leachate composition mg/L			
	Mg	Si	K	Na
0.0	0.004	57.72	2.05	19.47
1.3	0.004	63.67	2.54	23.09
4.0	0.036	67.45	2.71	25.45
13	0.46	41.68	2.05	21.30
40	31.55	26.13	1.33	14.55
400	399.6	22.13	1.45	13.78

TABLE 3
Leaching of Pyrex Glass in Tris-buffered Mg Solutions

Leachant composition mg/L		Leachate composition mg/L		
Mg	Mg	Si	K	Na
0.0	0.00	13.54	2.29	2.48
0.1	0.07	13.16	2.28	2.46
1.0	0.80	12.95	2.26	2.45
10.0	10.06	9.70	2.45	1.84

TABLE 4
Leaching of Soda-Lime Glass in CAPS-buffered Al Solutions

Leachant composition mg/L	Leachate composition mg/L			
	Al	Si	K	Na
0.00	0.07	159.1	10.6	174.3
0.02	0.06	146.7	10.4	166.4
0.05	1.06	27.75	1.46	89.2
0.10	1.20	27.61	1.17	111.5
0.50	4.00	19.79	1.98	98.84

Table 5

Compositions of Spent Pre-treatment Solutions, mg/L

Glass -----	Element -----	pH 5.5 -----	pH 8.1 -----
None	Na	0.429	0.078
	Mg	16.9	17.4
Fused quartz	Na	0.493	0.077
	Mg	15.6	14.8
Pyrex	Na	1.55	1.36
	Mg	15.5	15.4
Soda-lime	Na	7.96	8.96
	Mg	14.5	15.3
SRL-131	Na	14.5	13.6
	Mg	10.9	12.6
WV-205	Na	8.81	8.46
	Mg	10.2	11.8

Table 6

Compositions of DI Water Leachates of Pre-treated Glass Samples,
mg/L

Glass	Element	ppm		
		Untreated	pH 5.5	pH 8.1
Fused quartz ₁	B	0.080	0.004	0.005
	Si	1.31	1.51	0.486
Fused quartz ₂	B	0.074	0.001	0.003
	Si	1.69	1.25	0.756
Pyrex ₁	B	0.208	0.080	0.049
	Si	0.330	0.238	0.105
Pyrex ₂	B	0.201	0.067	0.051
	Si	0.321	0.105	0.099
Soda Lime ₁	B	0.133	0.012	0.024
	Si	1.99	0.139	0.242
Soda Lime ₂	B	0.112	0.008	0.006
	Si	1.98	0.122	0.122
SRL-131 ₁	B	0.931	0.375	0.363
	Si	1.21	0.671	0.597
SRL-131 ₂	B	0.967	0.353	0.407
	Si	1.19	0.602	0.661
WV-205 ₁	B	0.756	0.301	0.291
	Si	0.885	0.550	0.557
WV-205 ₂	B	0.827	0.287	0.281
	Si	0.986	0.562	0.571

TABLE 7
Compositions of Leached Glasses by SEM/EDX

Element	Concentration, atom %			
	Experiment A		Experiment B	
	No Mg		1.6 mg/L Mg	
	Bulk 25u	Surface 3u	Bulk 25u	Surface 3u
Na	6.23	0.80	9.06	7.61
Mg	2.19	0.19	3.01	2.57
Al	0.95	0.54	1.12	1.21
Si	25.95	28.41	24.39	25.05
K	0.58	1.06	0.38	0.48
Ca	2.59	5.12	1.93	2.28
O	61.51	63.88	60.11	60.81

TABLE 8
Compositions of Glasses for Magnetic Susceptibility Studies

Glass	SiO ₂	Oxide concentration, wt. %				Fe(II)/Fe(III)	
		Fe ₂ O ₃	R ₂ O	B ₂ O ₃	Al ₂ O ₃	Wet	Moss
A	44.1	11.5	19.5	10.0	6.1	0.03	0.01
B	44.6	11.7	20.2	9.9	5.5	0.01	0.06
C	44.5	11.3	19.2	10.4	5.3	0.25	0.39
D	46.2	11.7	20.1	9.9	3.4	low	
E	44.0	11.0	20.1	10.3	5.3	0.12	0.29
F	45.2	11.8	22.0	10.0	3.3	low	
G	43.9	13.6	19.9	9.9	3.7	low	

R₂O = Total alkali oxides (calculated as Na₂O)

Fe₂O₃ = Total iron oxides (calculated as Fe₂O₃)

Wet = Wet chemical analysis (1,10-phenanthroline spectrophotometry after dissolution)

Moss = Mossbauer spectroscopy

Glass D is partially devitrified, containing approximately 20 vol. % of spinel, (Ni,Fe)Fe₂O₄

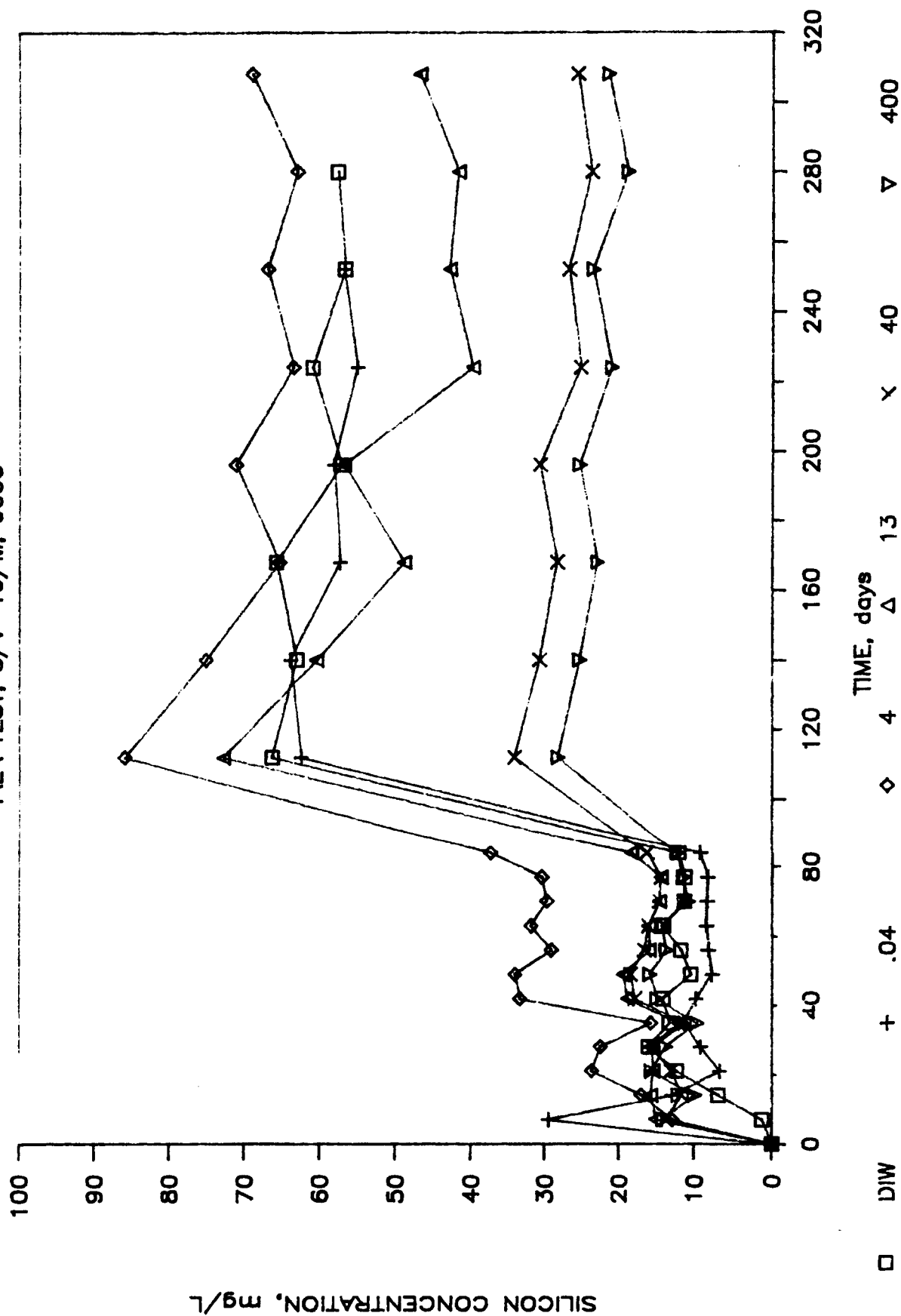
TABLE 9
Magnetic Susceptibilities of Fe-containing Borosilicate Glasses
(~~5~~-6 emu/g)

Temp. K	Field kOe	A	B	C	Glass D	E	F	G
77	0.225				1541	271		
77	0.4	202	179		1178			69
77	0.6				1026	175		
77	0.8	159	140		903			
77	1.0	154			801	136		61
77	1.4	139			641			61
77	2.0	114	103	65		104	61	60
77	2.7							61
77	3.2		93	63		100	61	60
300	0.225				1314	209		
300	0.4	147	131		1038			
300	0.6				883	114		28
300	0.8	105	90		759			
300	1.0	96			665	86		22
300	1.4	79			515			20
300	2.0	68	55	19		57	20	19
300	2.7							18
300	3.2		42	18		41	19	18

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Fig. 1 LEACHING OF SODALIME IN Mg SOLUTIONS

1¹A TEST, S/V=19/M, 90°C



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Fig. 2
EXPERIMENT S087

40 PPM M5.

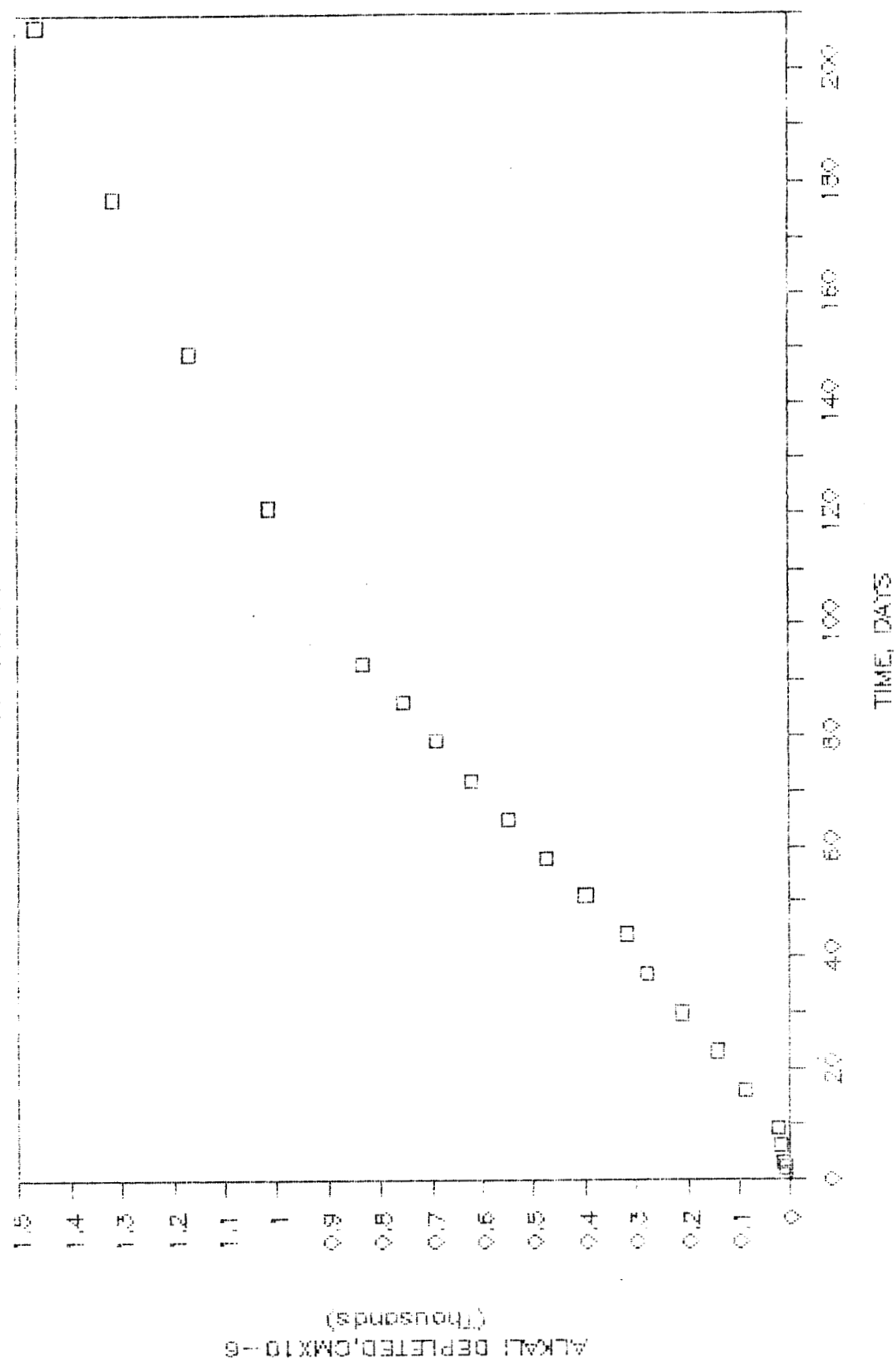
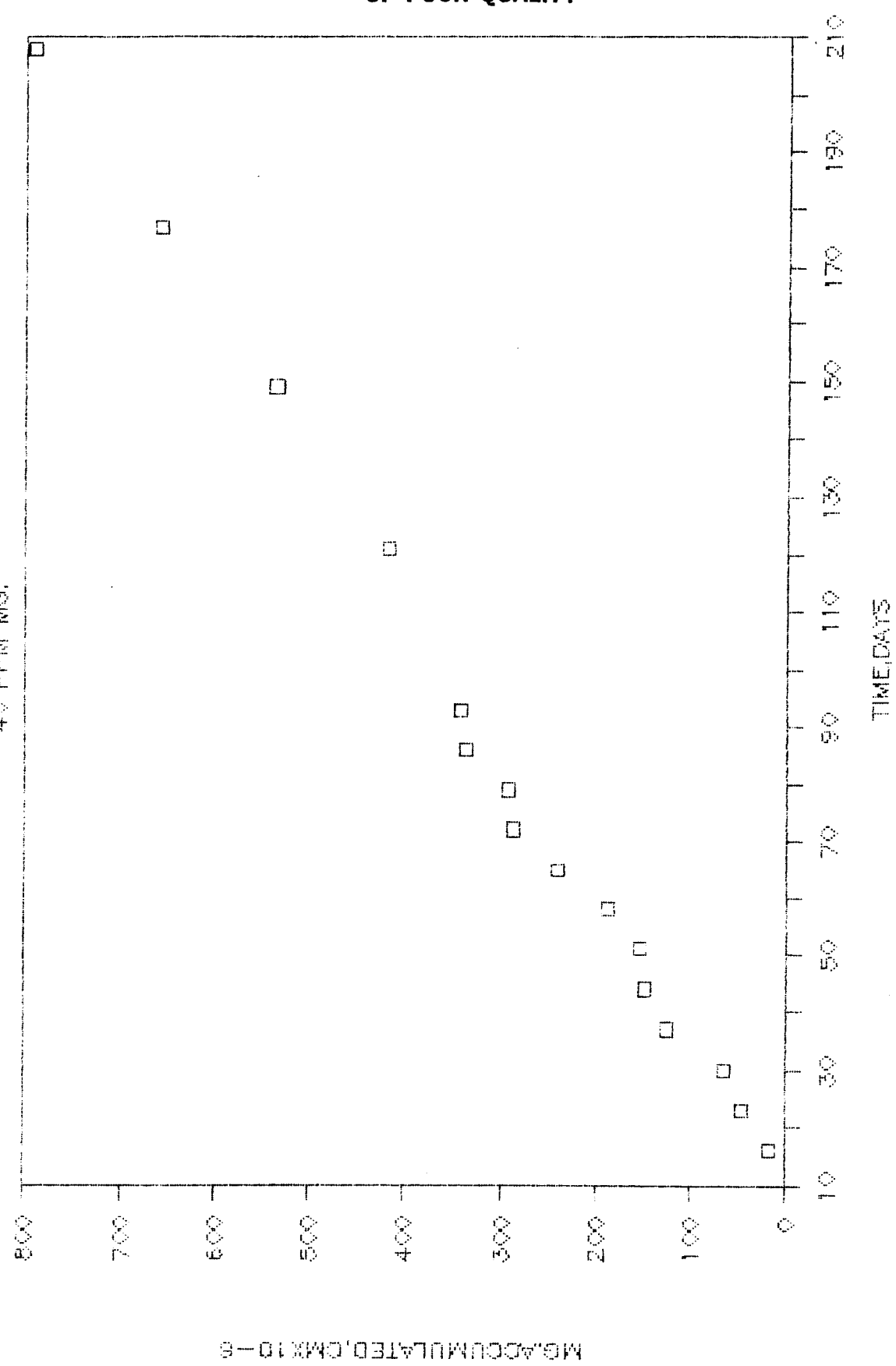


Fig. 3
EXPERIMENT S087

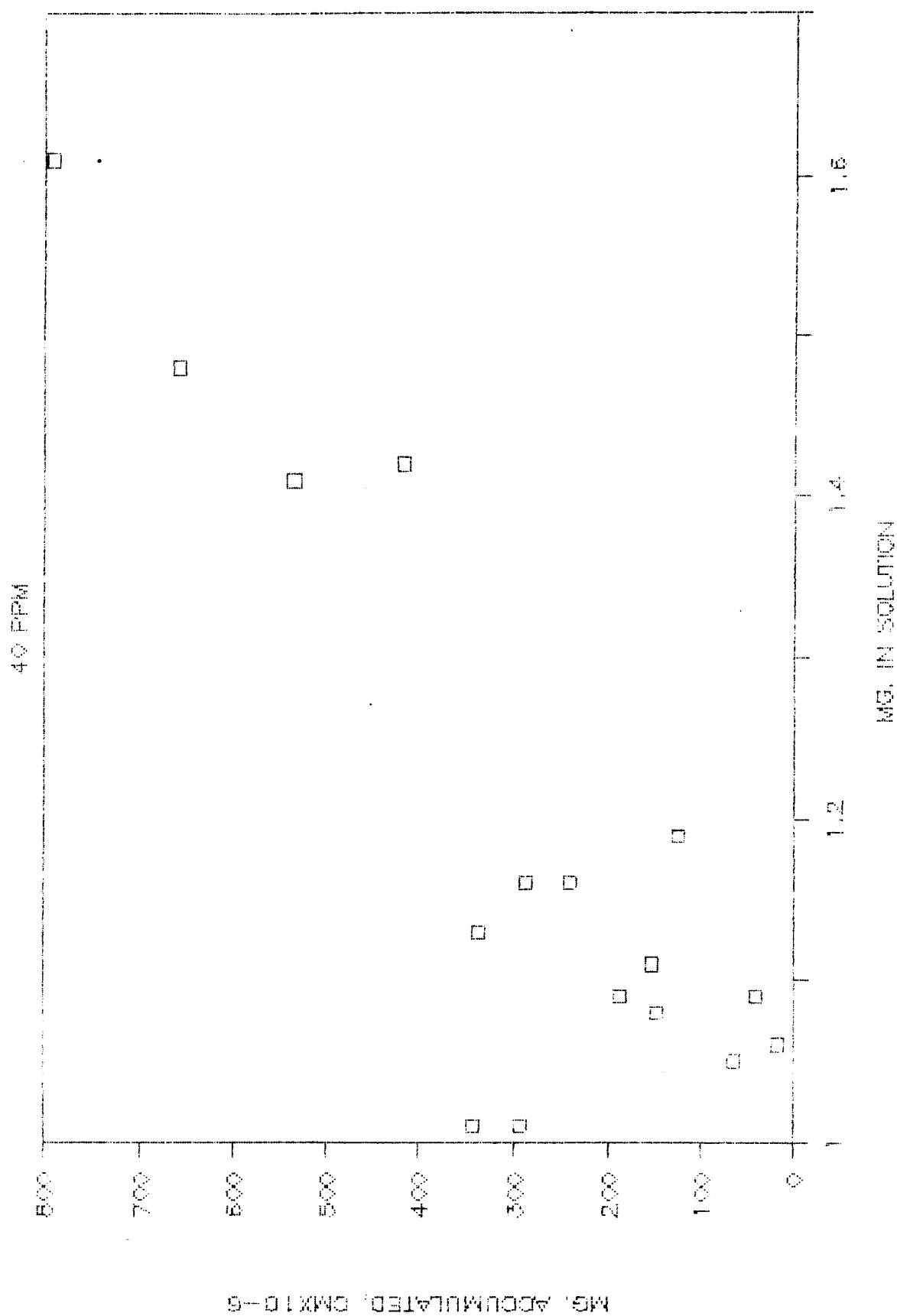
40 PPM MG.



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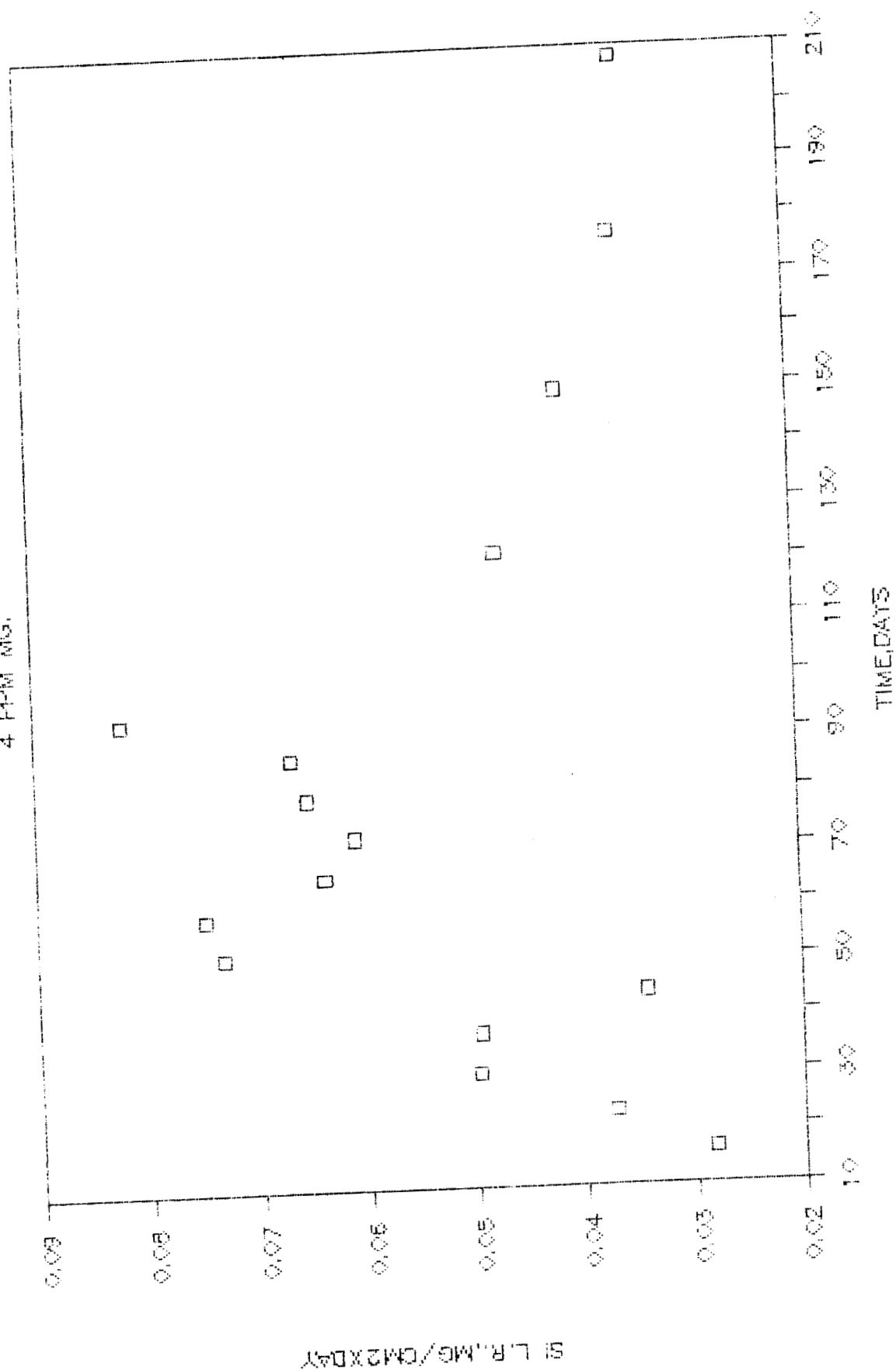
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Fig.4



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Fig. 5
EXPERIMENT S085
4 PPM MG.



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Fig. 6
EXPERIMENT S087

40 PPM MG.

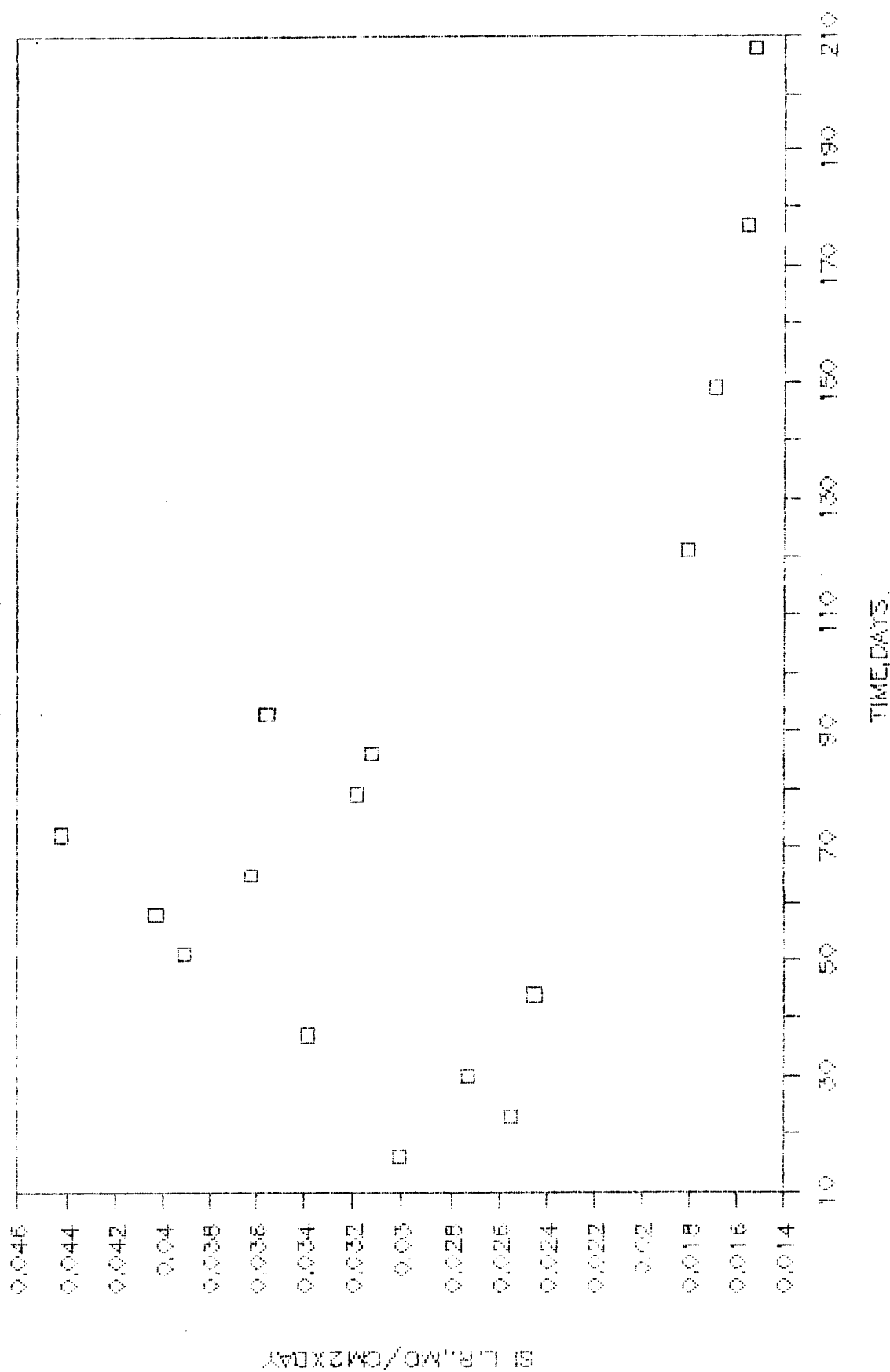


Fig. 7
EXPERIMENT S085
4 PPM

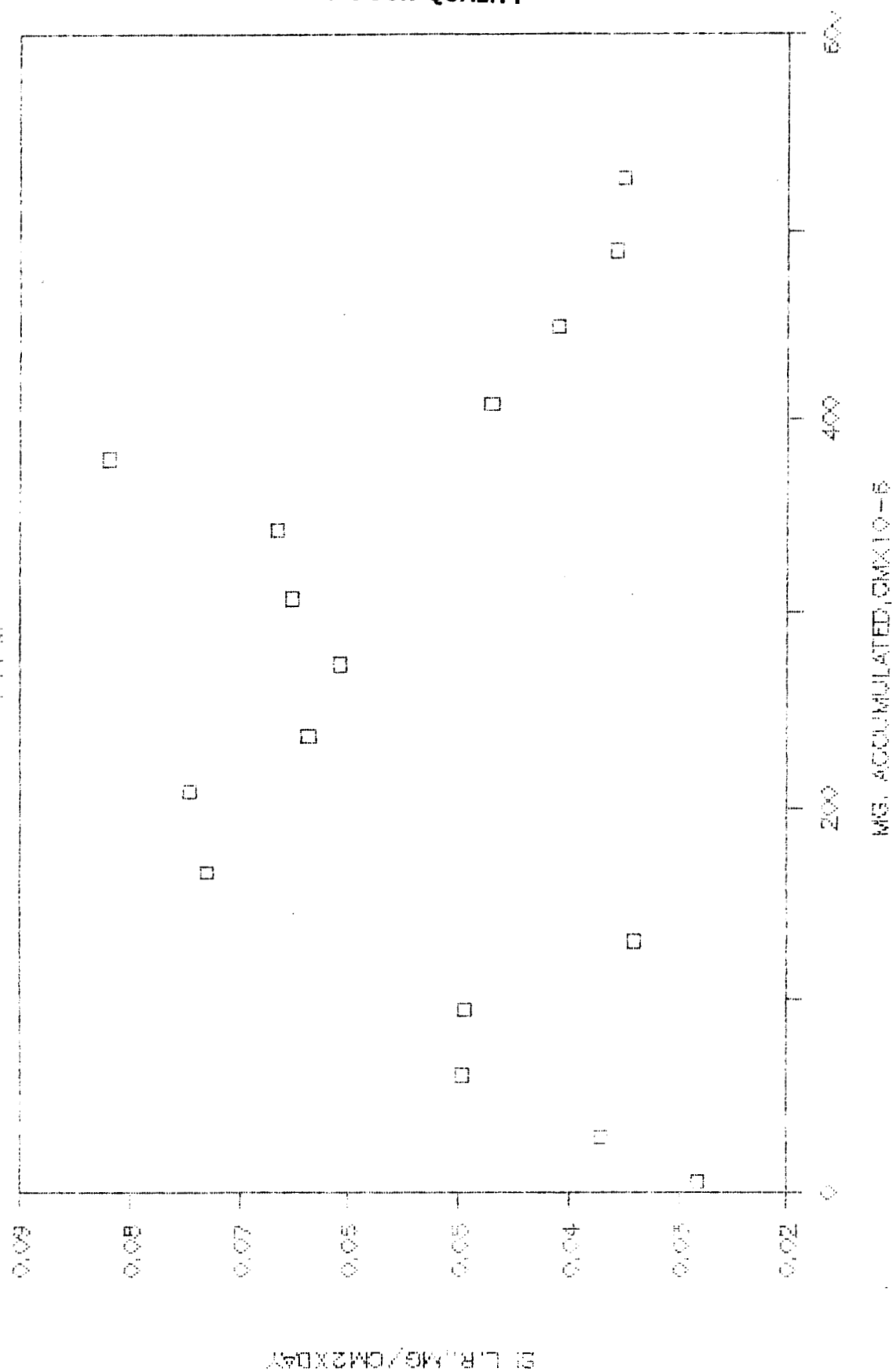


Fig. 8
EXPERIMENT S087

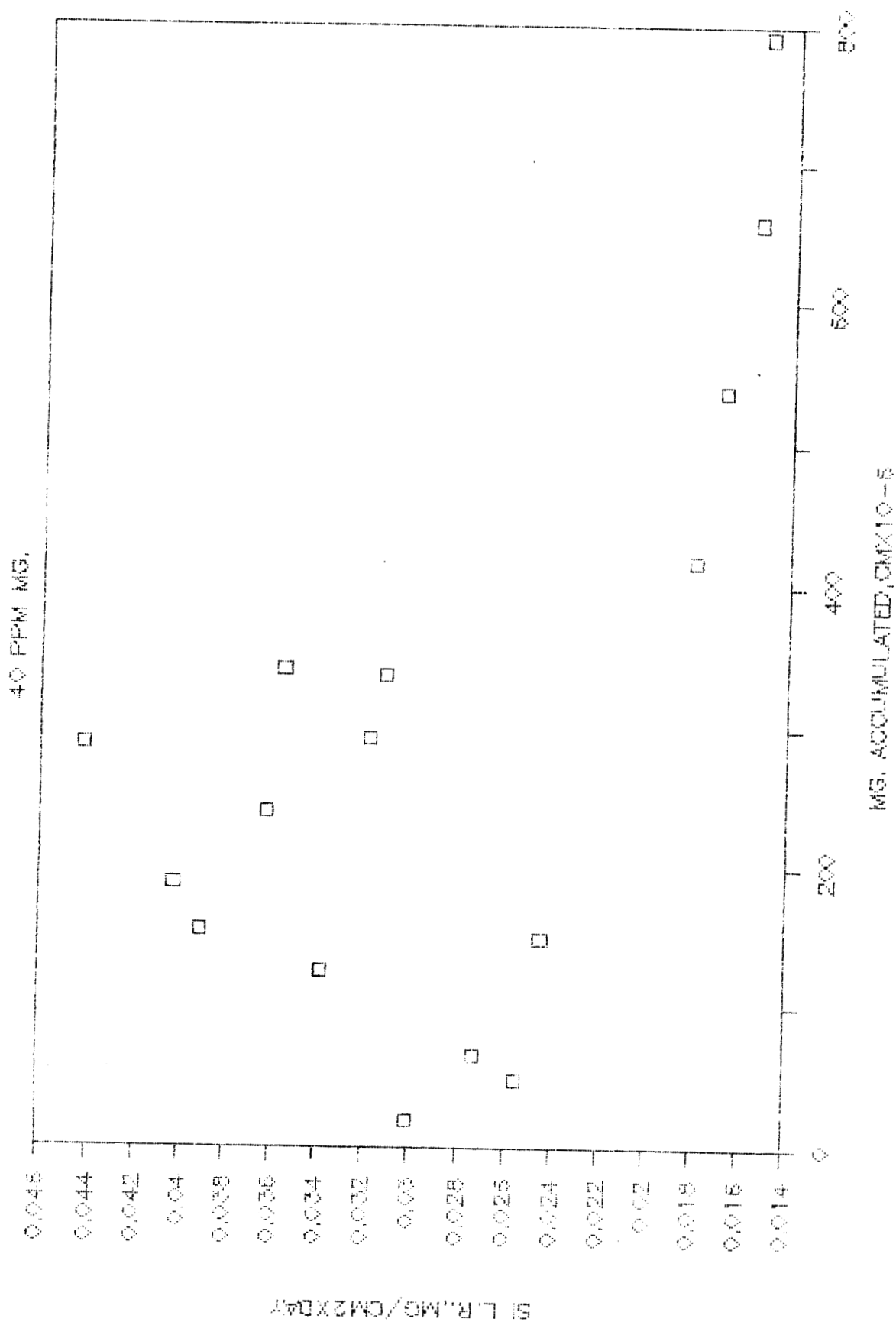
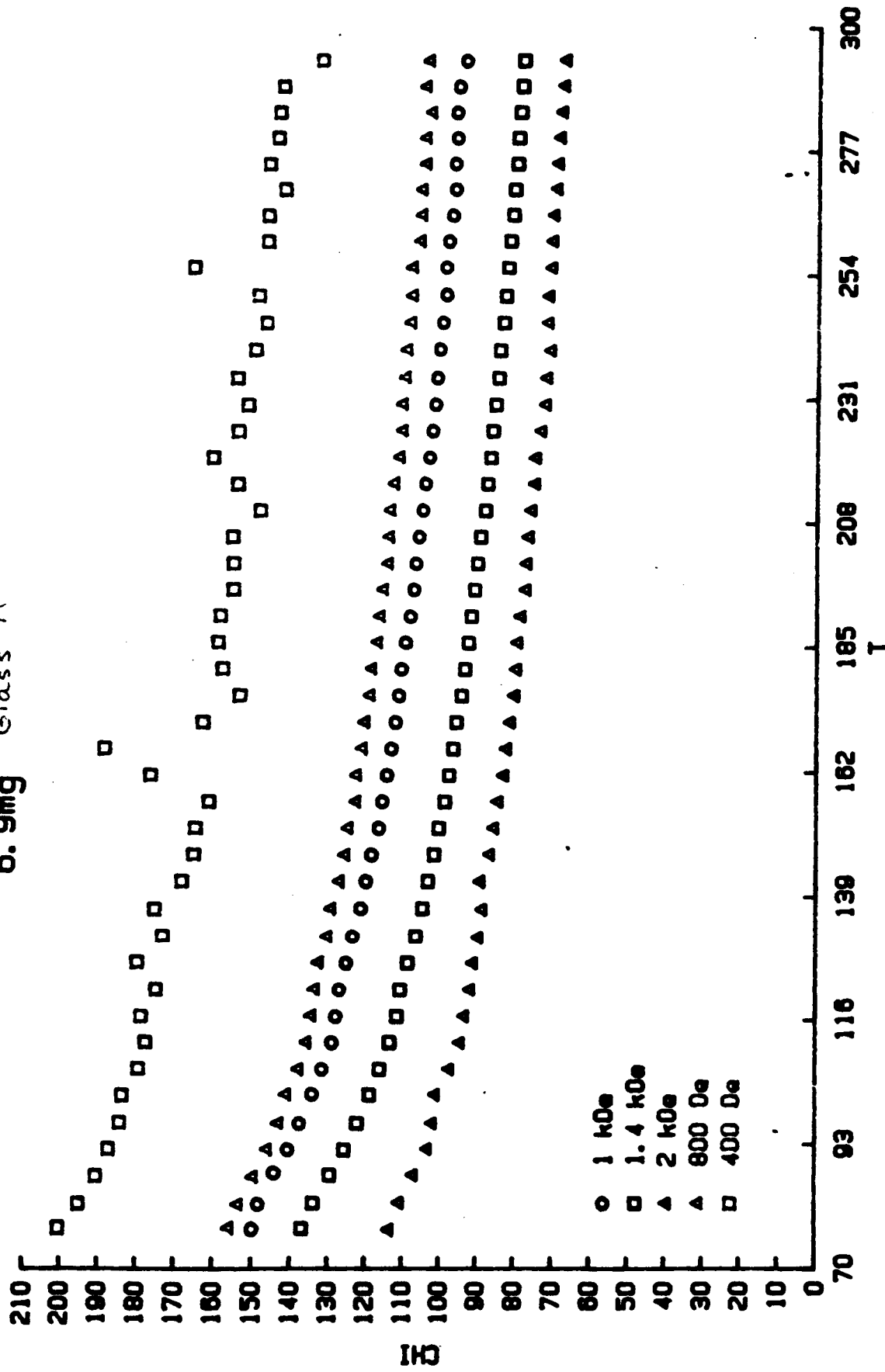


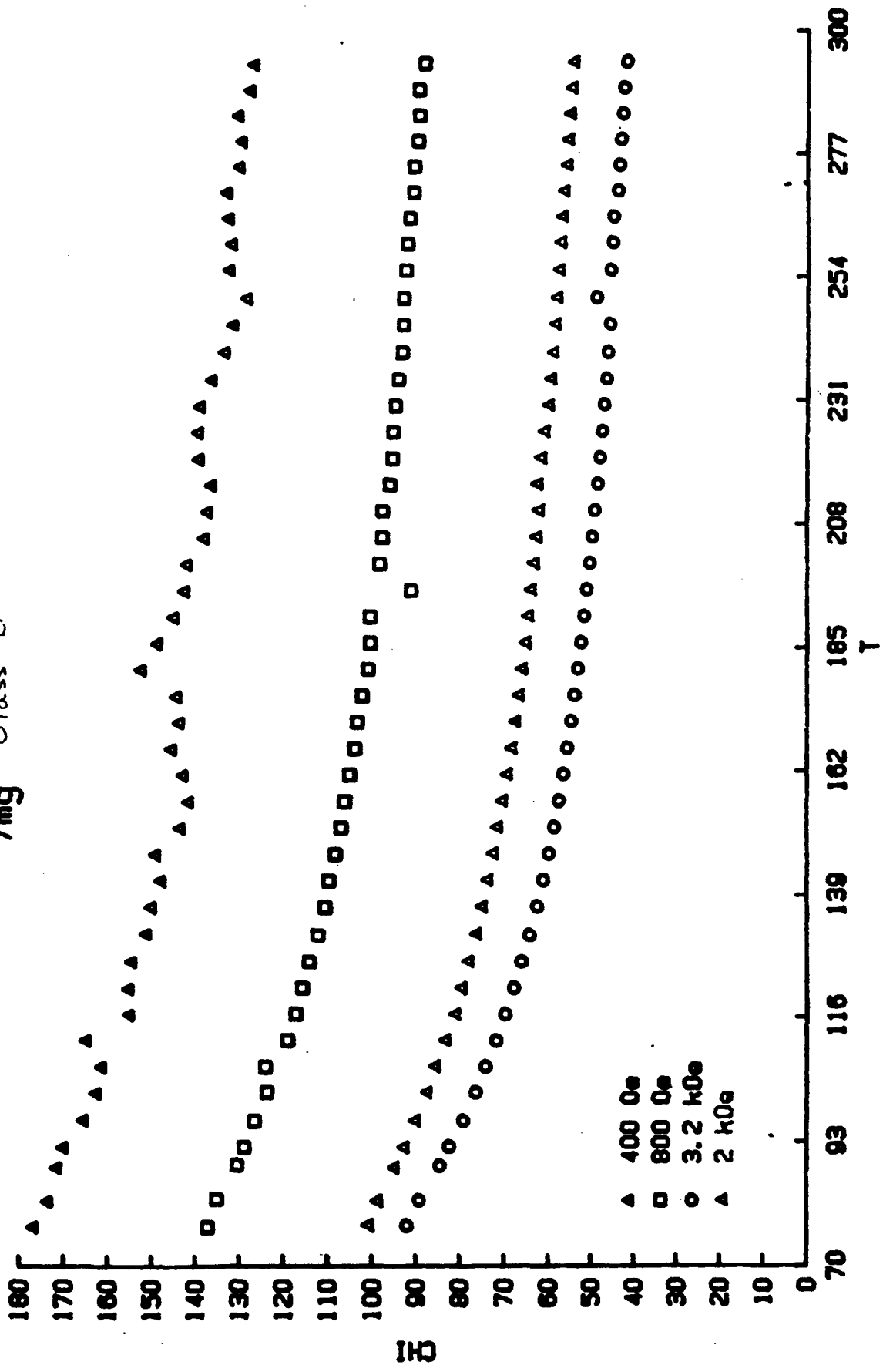
Fig. 9a

6.9mg Glass A



corr.-63a, T run: Data/31082088 003 082088 001 091988 001 091988 003 091988 002

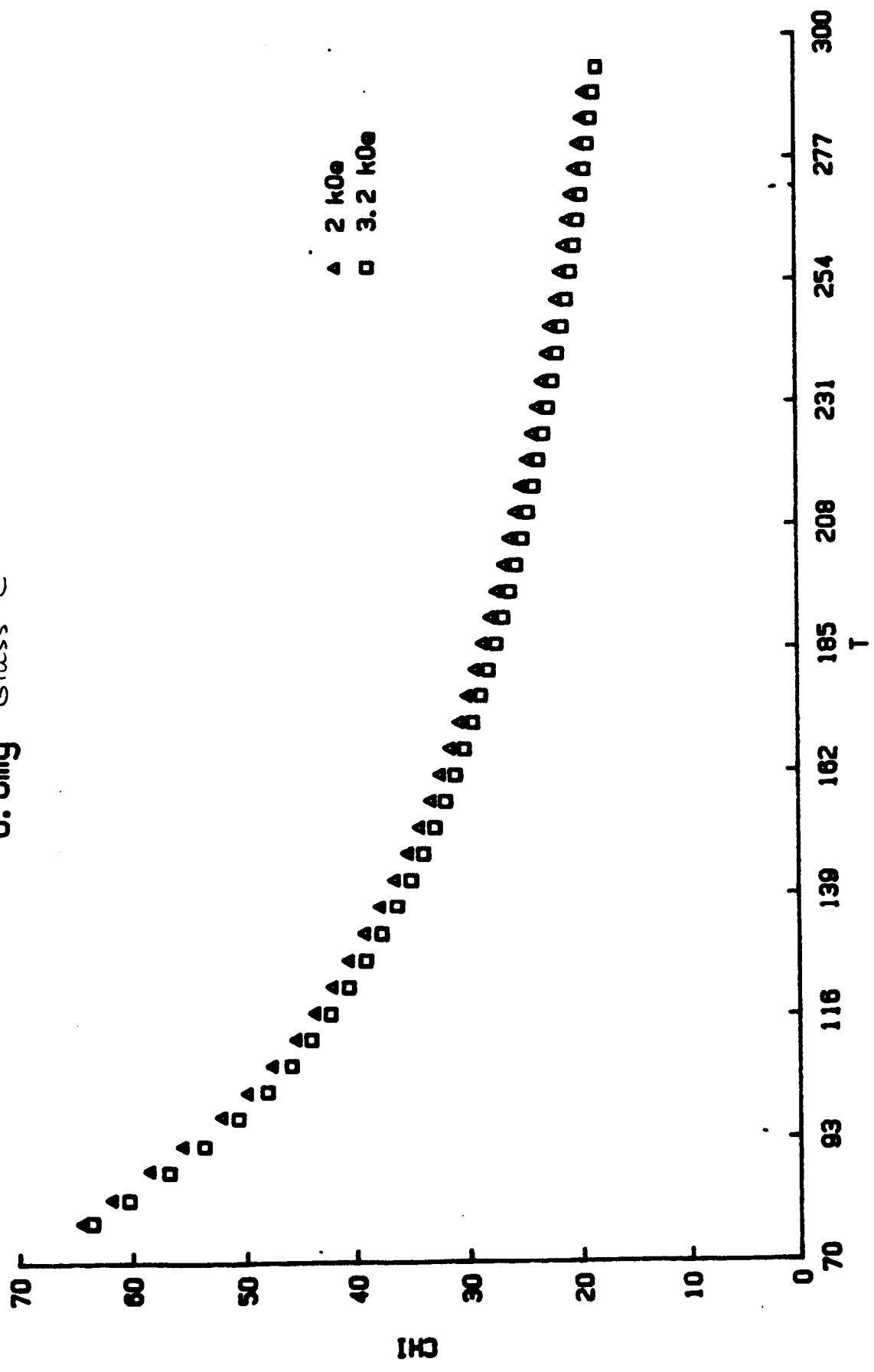
7mg Glass B



corr. = 1200, T run Data#3 [0922881 001 0922881 002 0922881 003 0922881 004]

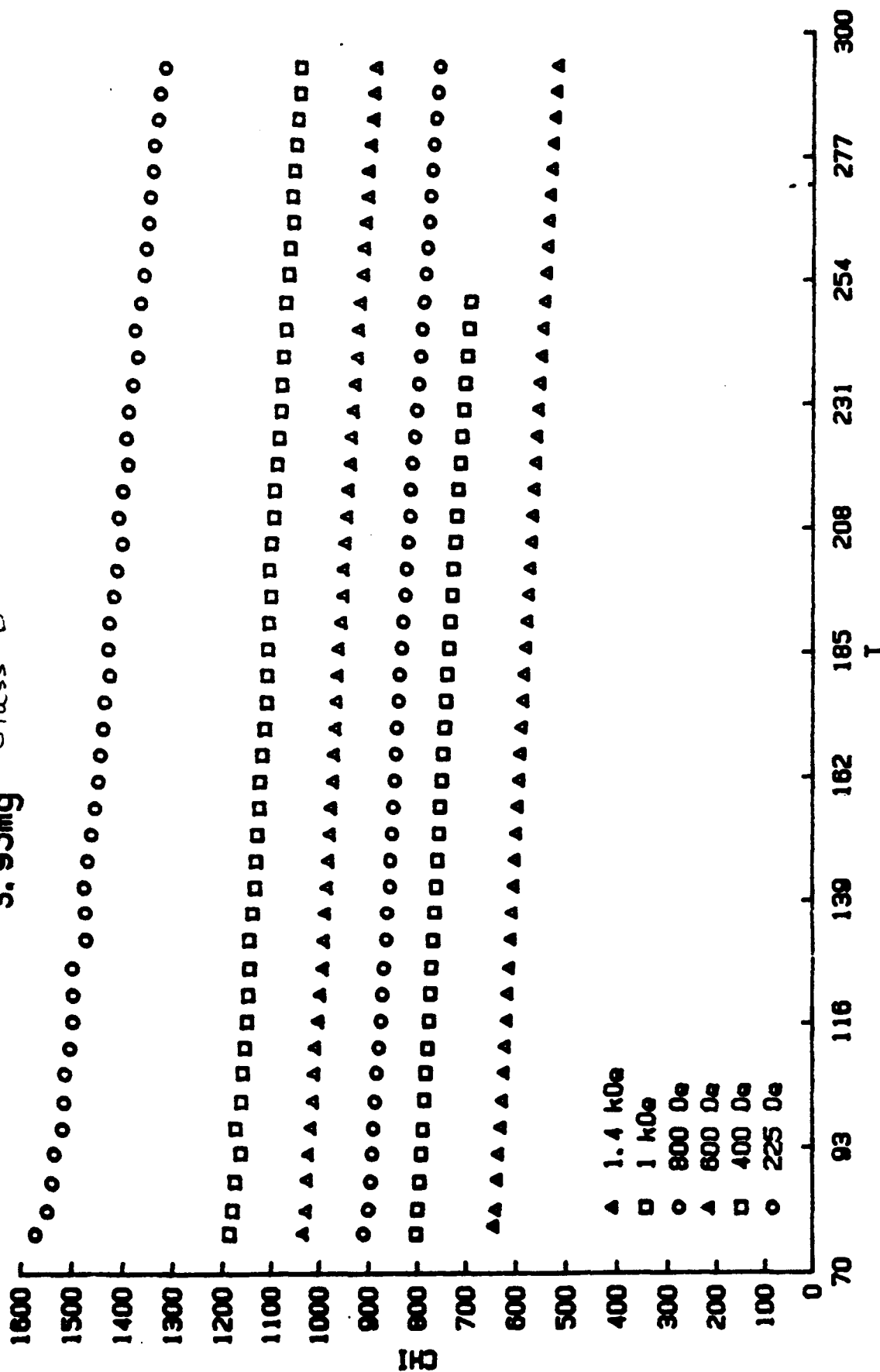
Fig. 9c

6.6mg Glass C



corr. -420, T run Date/3 [1013001 001 1013001/3A]

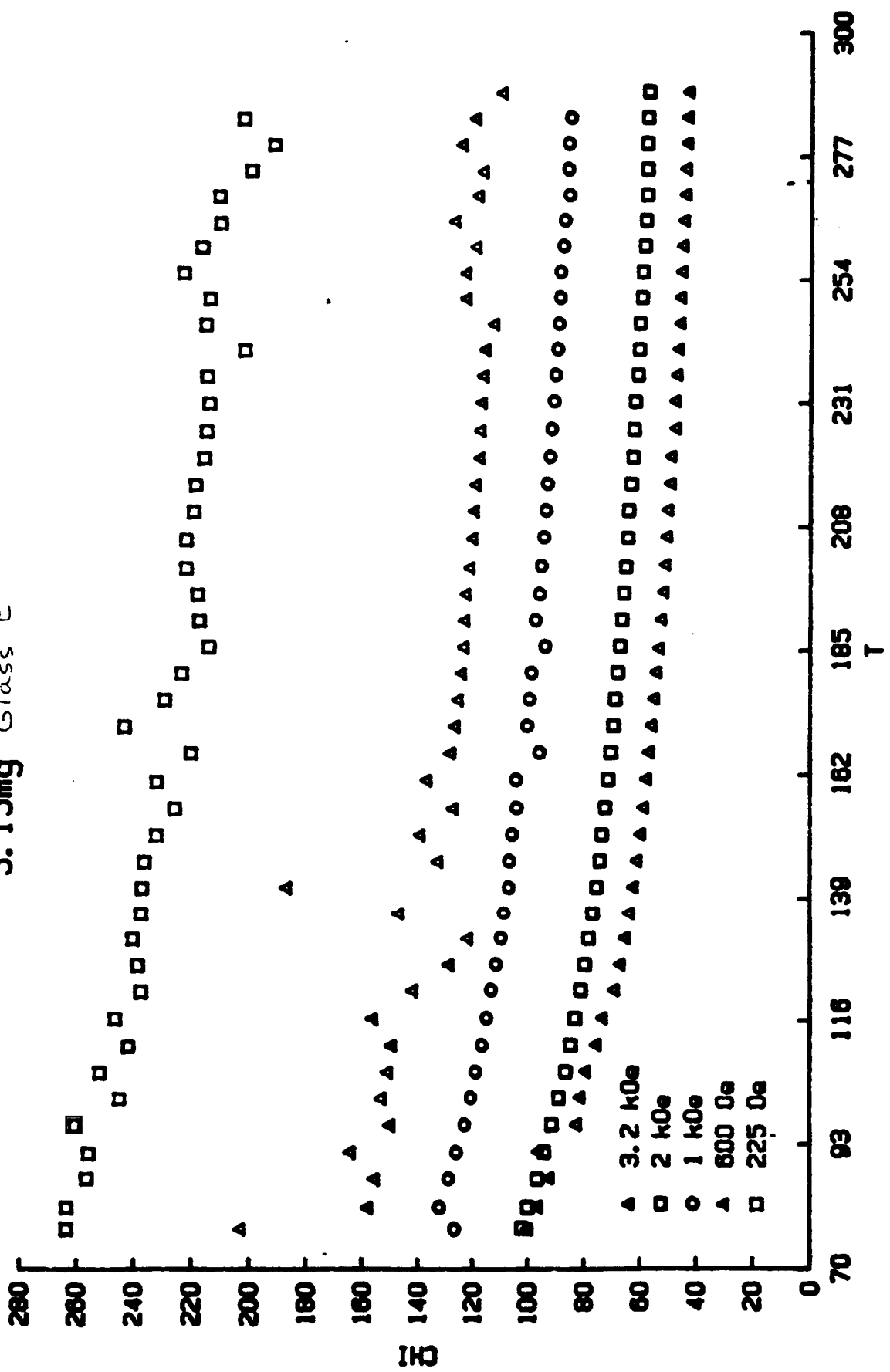
3.95mg Glass D



corr. ~420, T run [1010000 001 1010000 001-004 1020000 001] Date#3

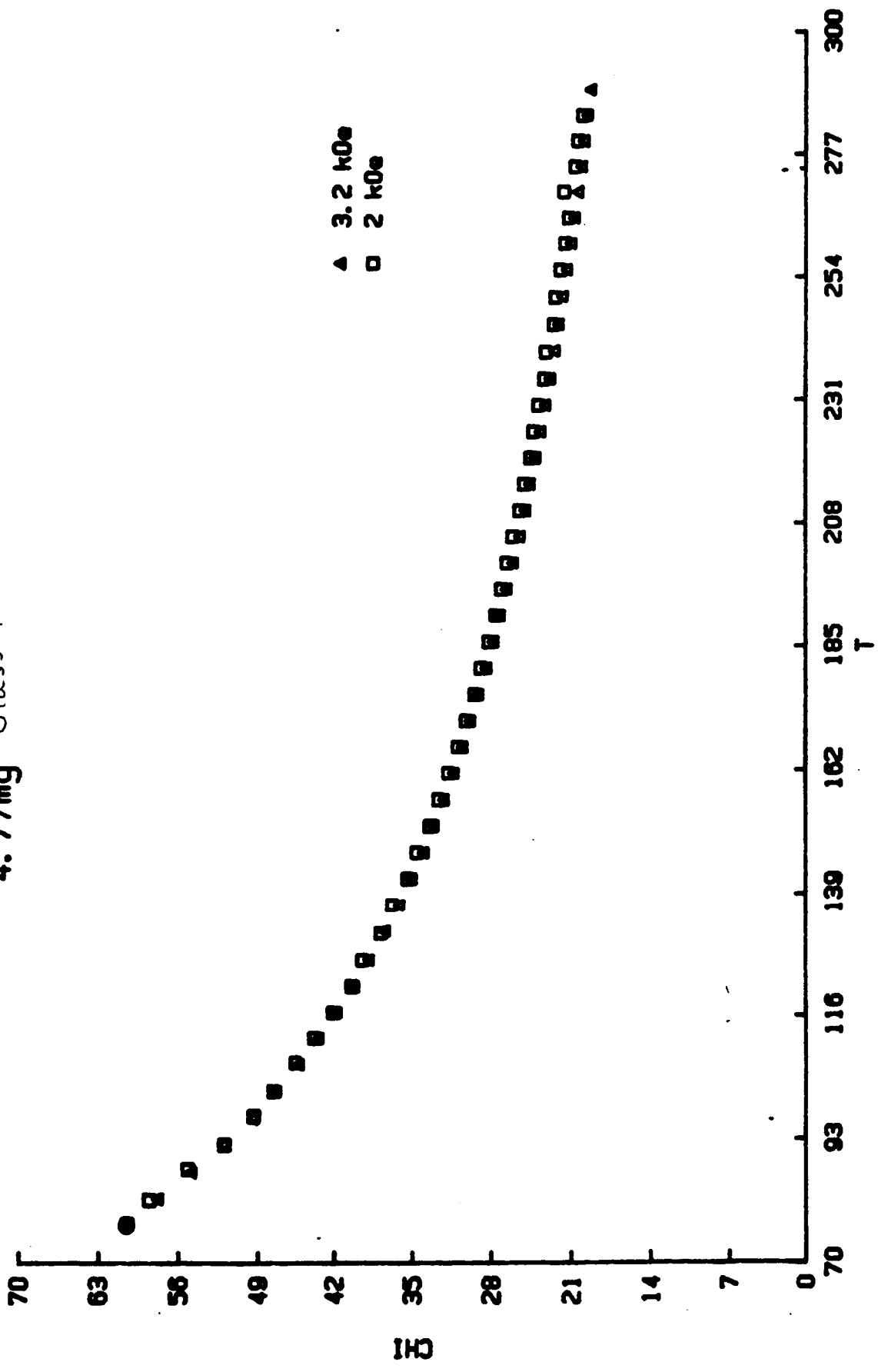
Fig. 9c

5.15mg Glass E



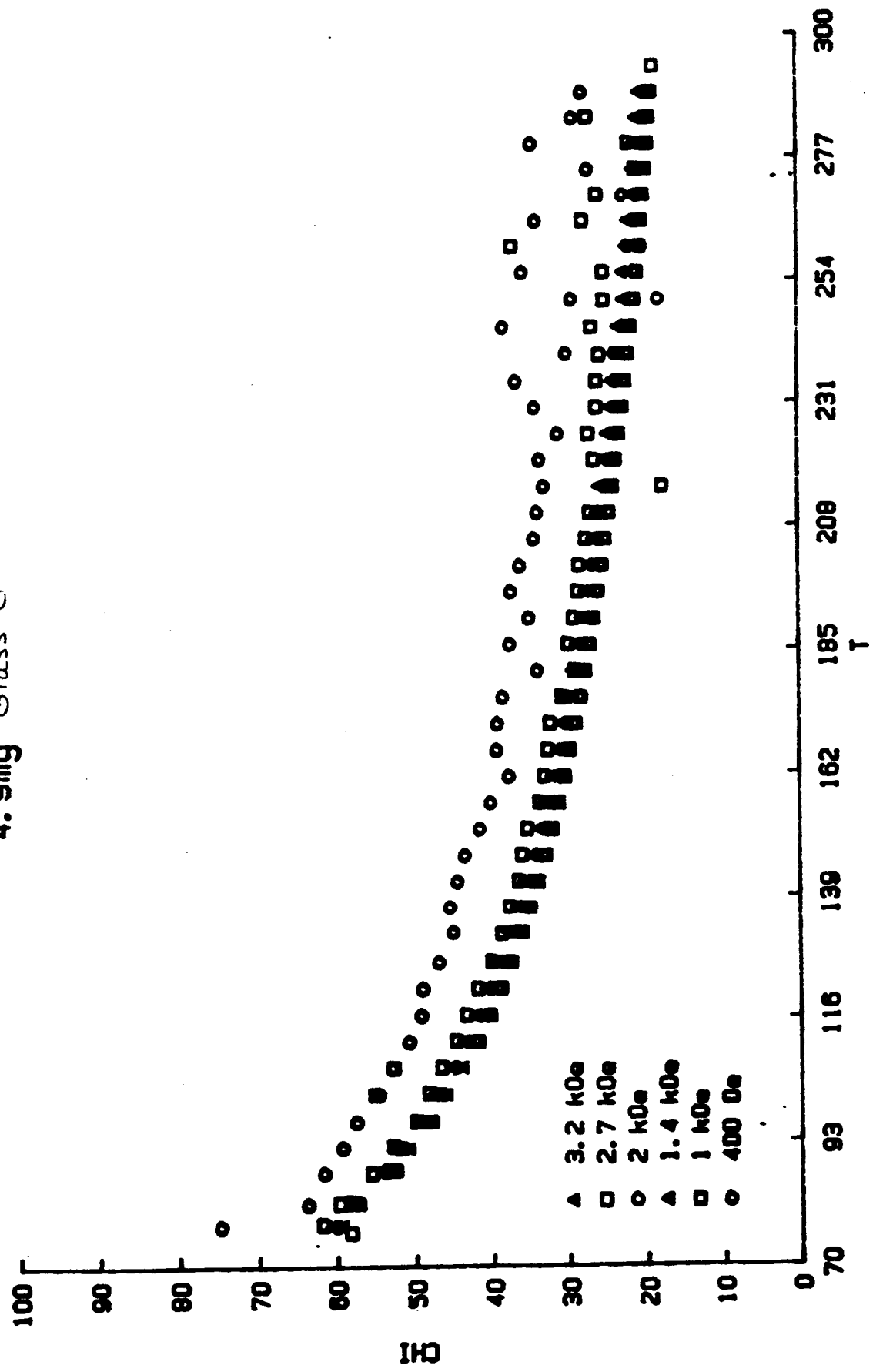
corr. -420; T run Date#3 (102588 001-005)

4.77mg Glass F



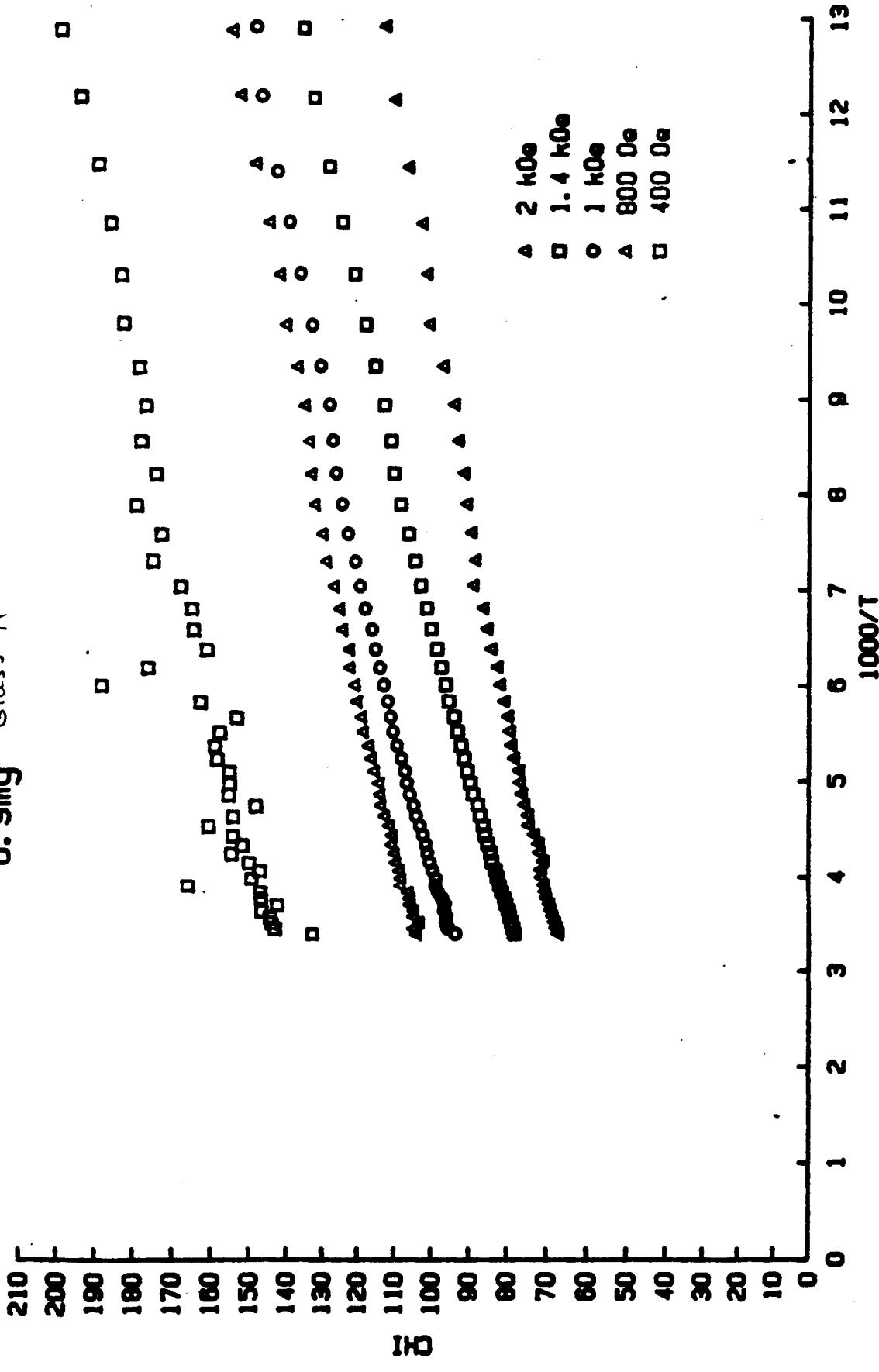
corr. -420; T run Data#3 (1027001 001-002)

4.9mg Glass G



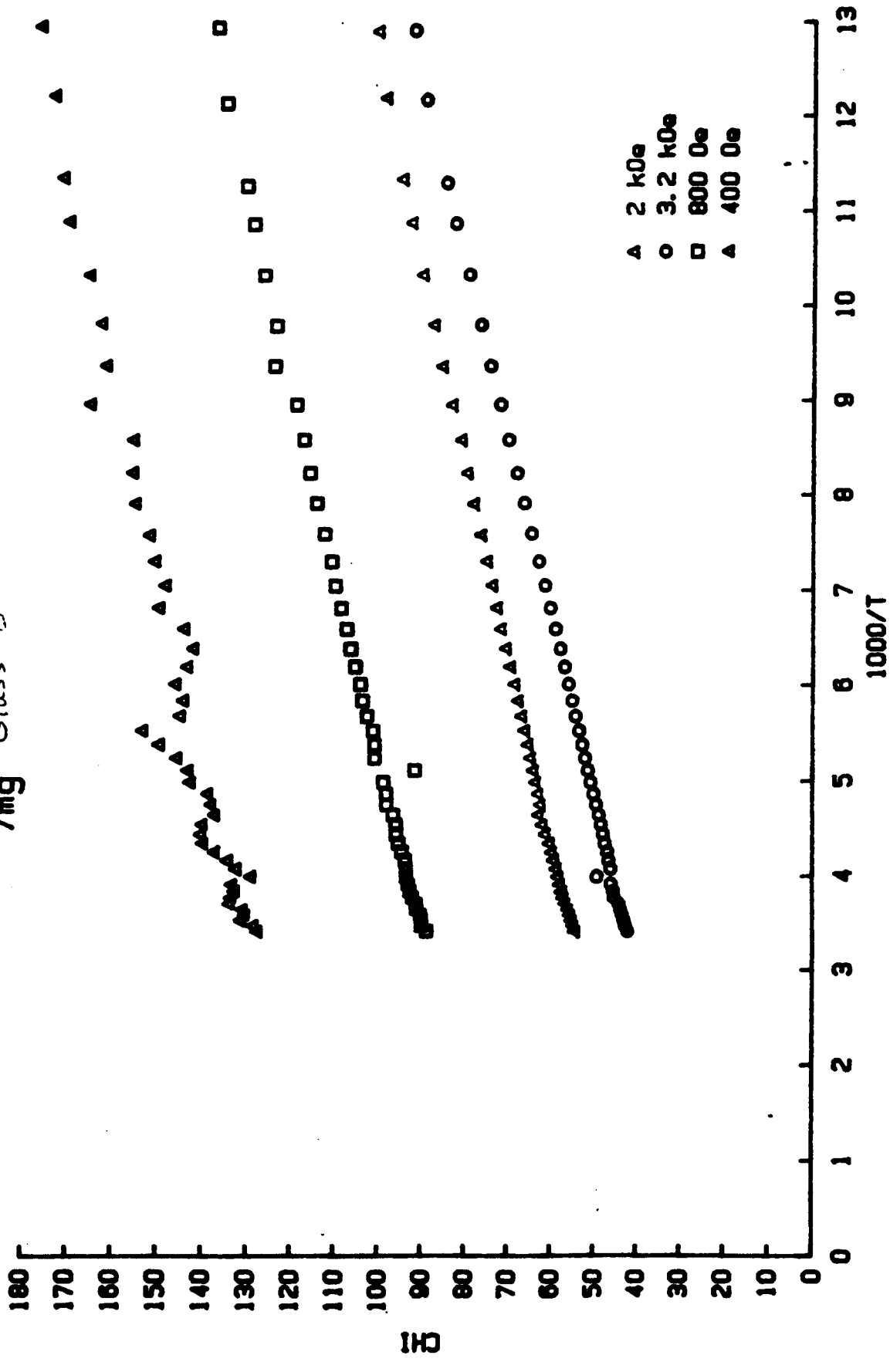
corr. -420, T runs Data#3 (1029001 001-004 1031001 001-002)

6.9mg Glass A



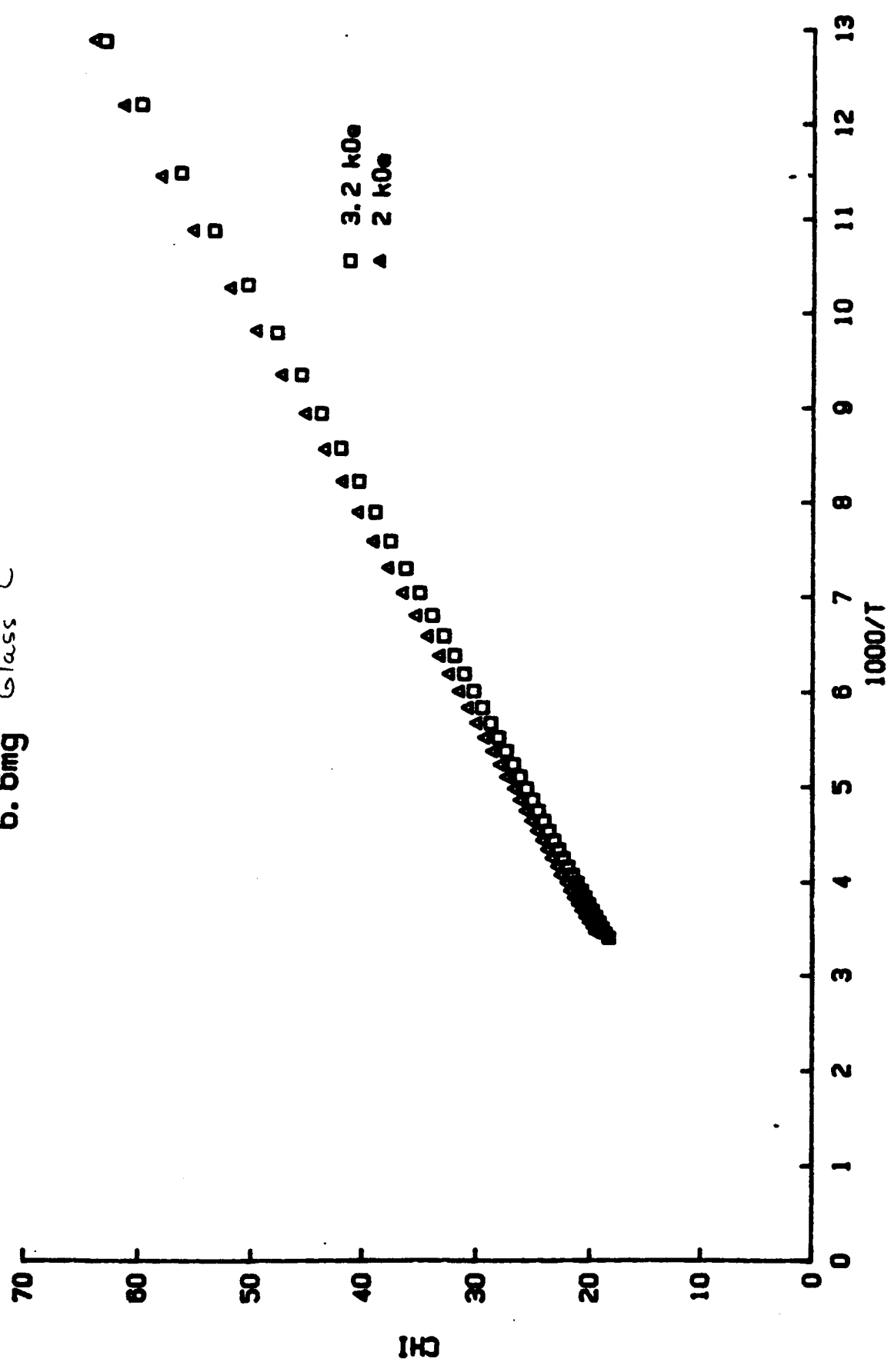
corr.-638 T run Date/9 082088 003 082088 001 091988 009 091988 002

7mg Glass B



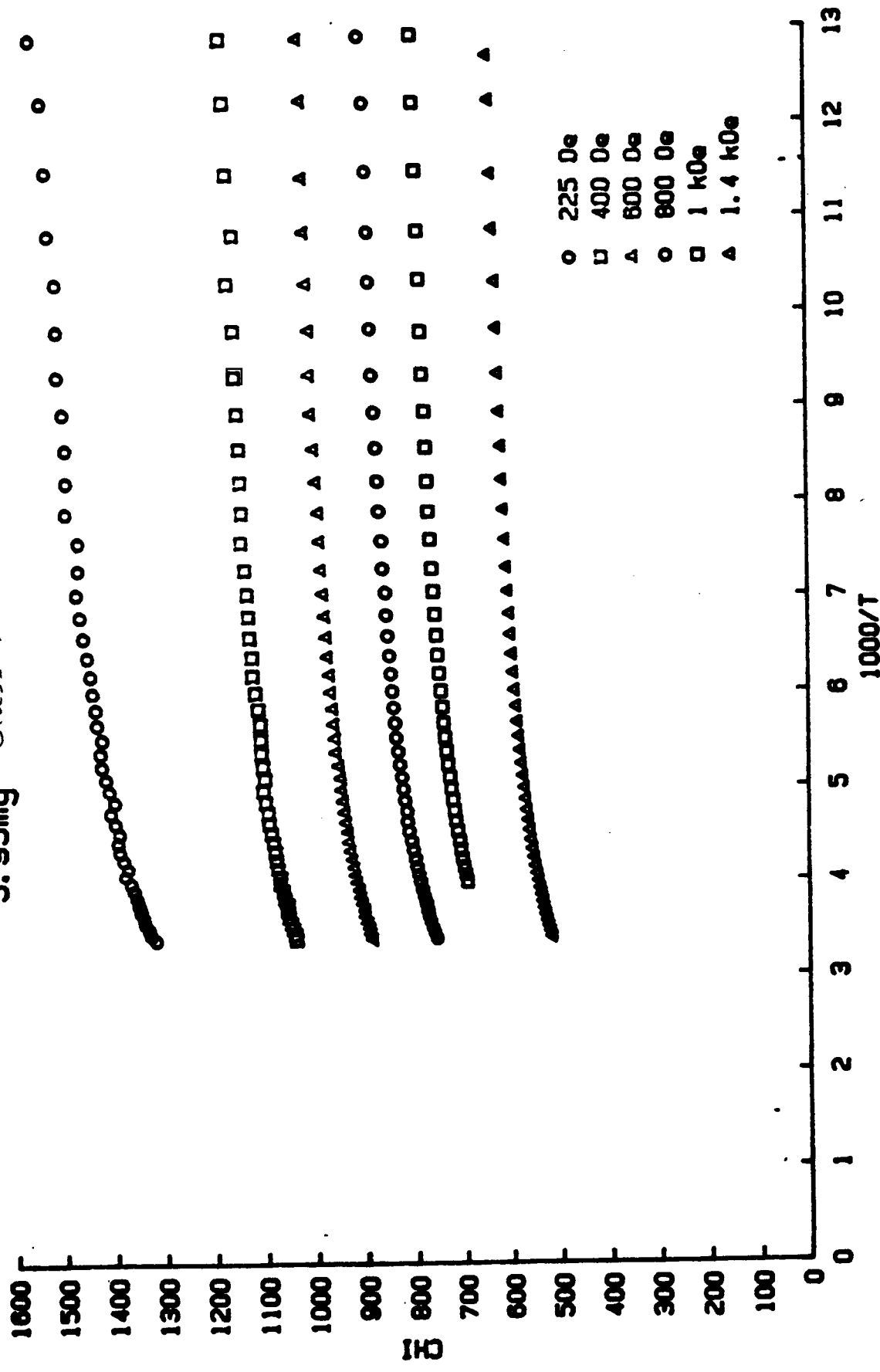
corr.-1200, T runs Data/3 [092288] 001 092288 002 092288 003 092288 004]

6.6mg Glass C



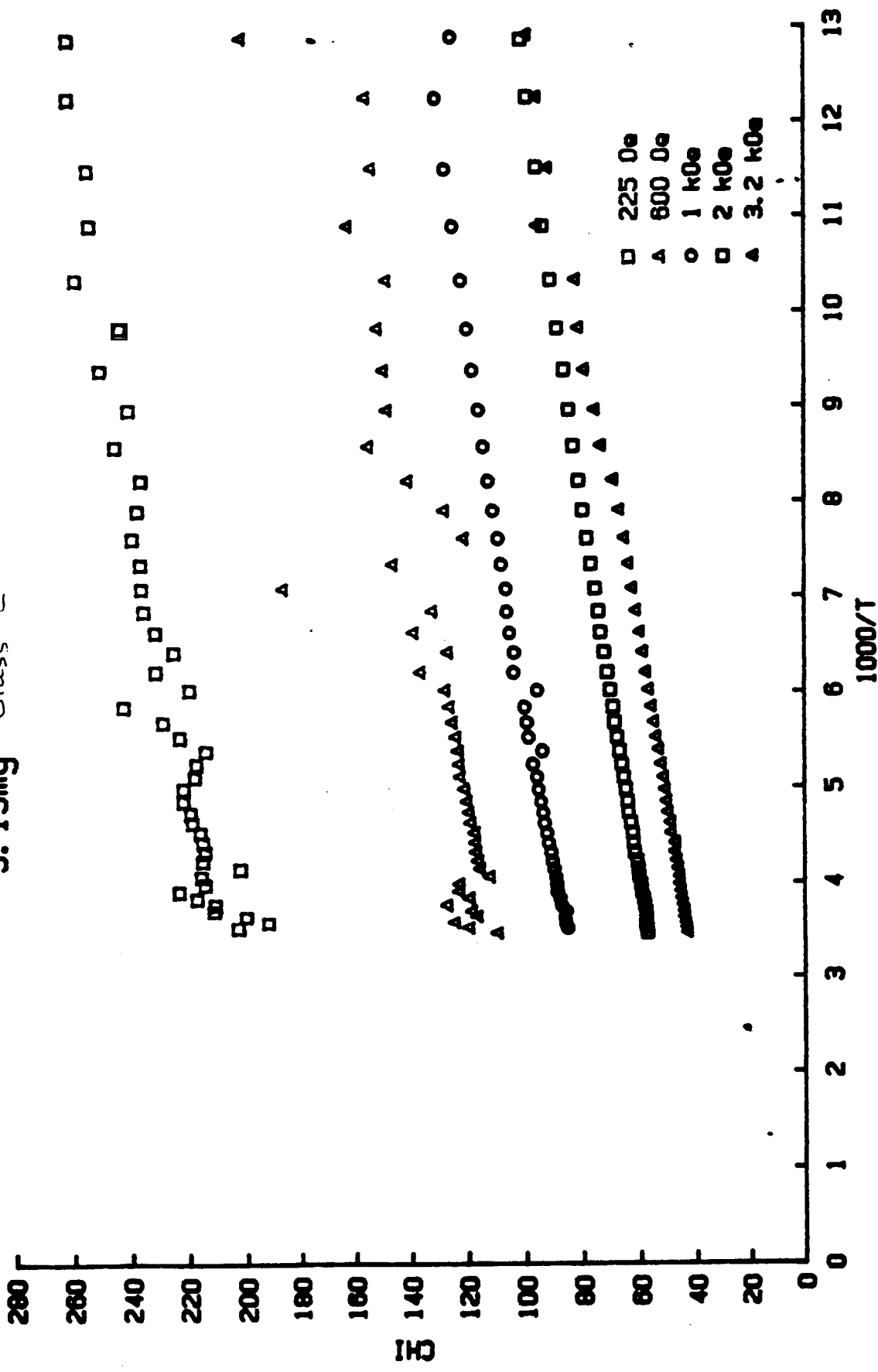
corr.=420, 1 run Data#3 (1013681 001 101368AN3A)

3.95mg Glass D



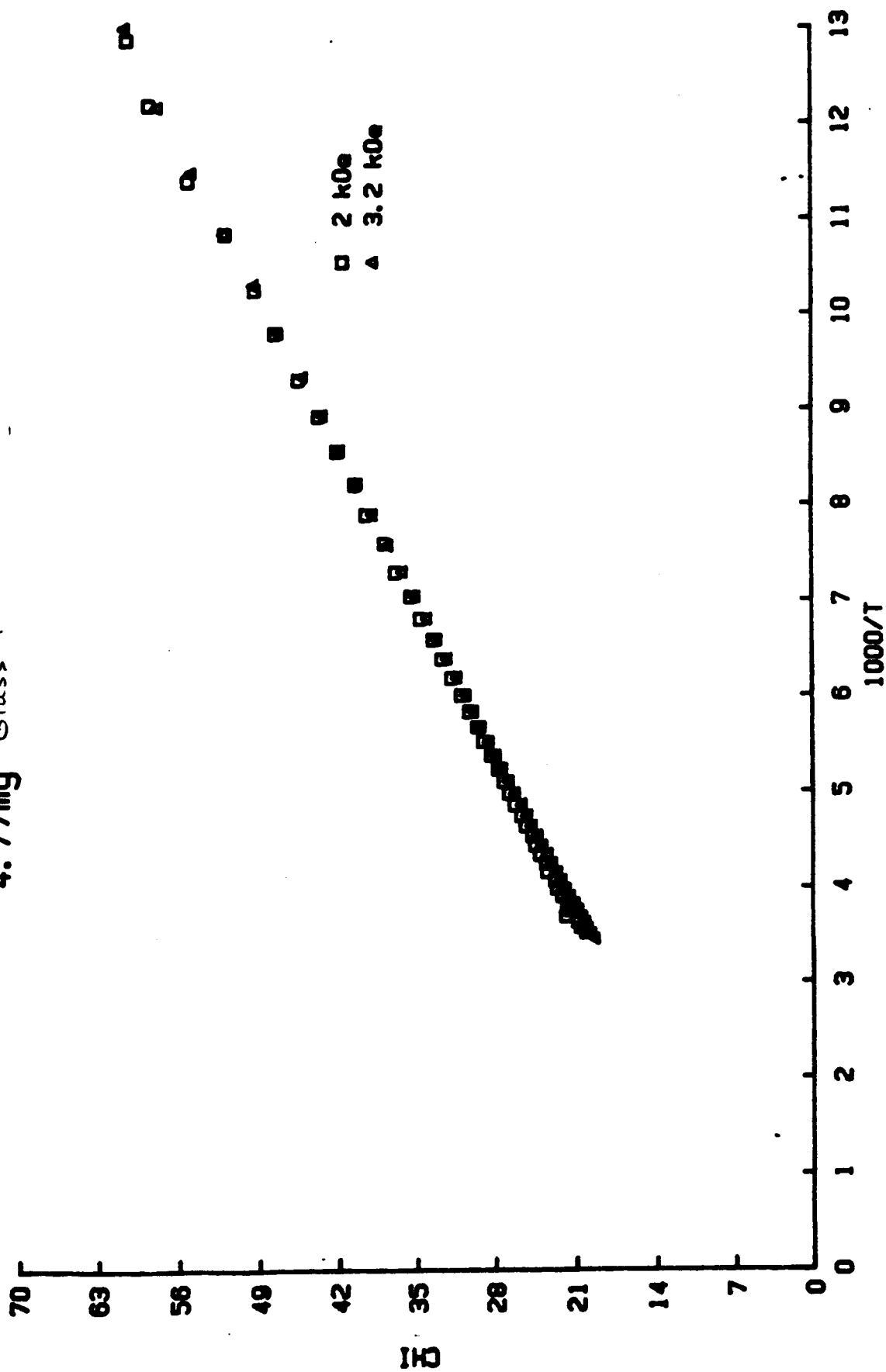
corr. -420; T run (101000 001 101000 001-004 102000 001) Data #3

5.15mg Glass E



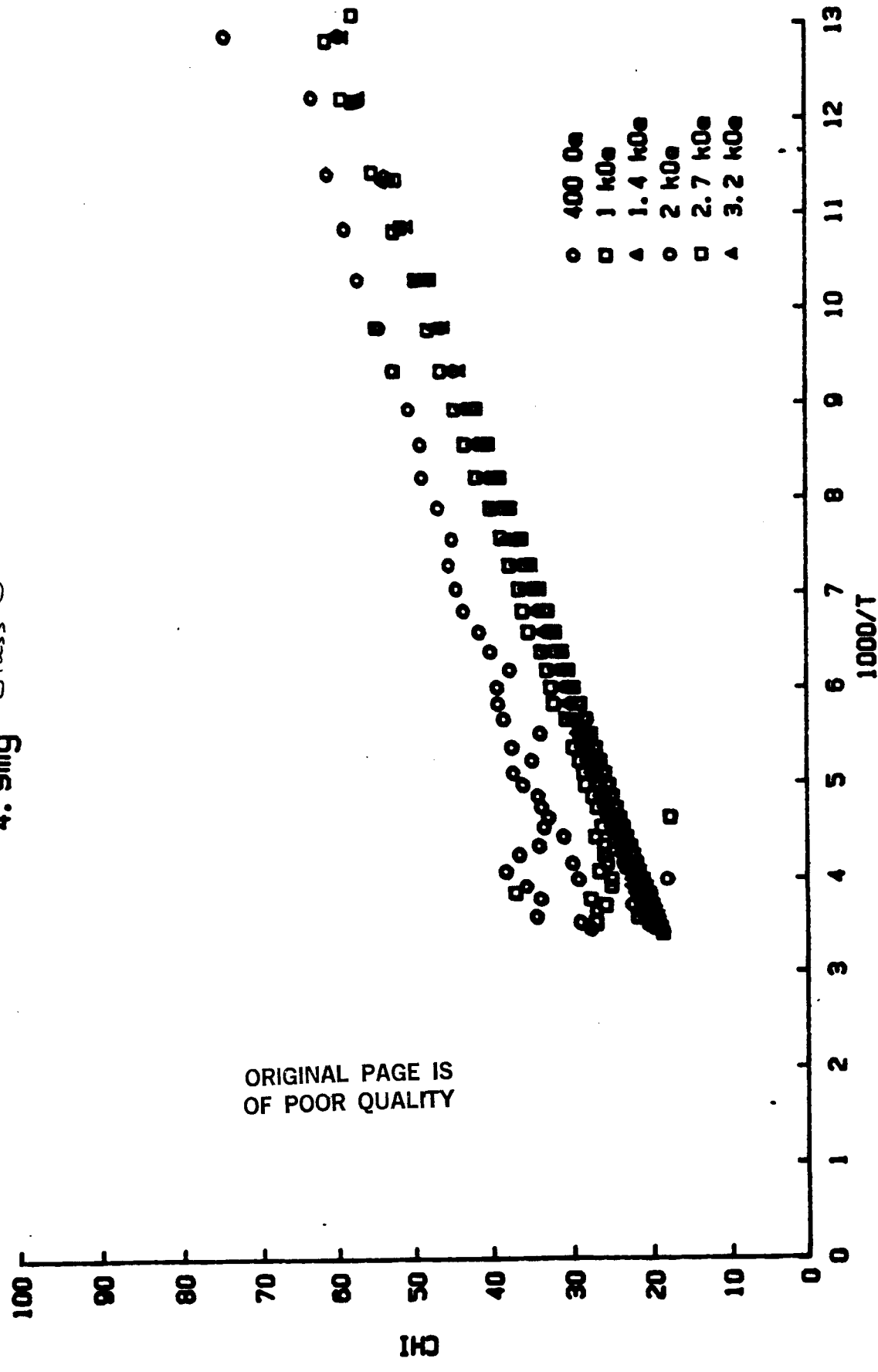
corr.-420, T pure Data#3 (102568 001-005)

4.77mg Glass F



corr. = 420, T run, Data#3 (1027981 001-002)

4.9mg Glass G



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corr.-420, T run Data#3 (1020001 001-004 1031001 001-002)